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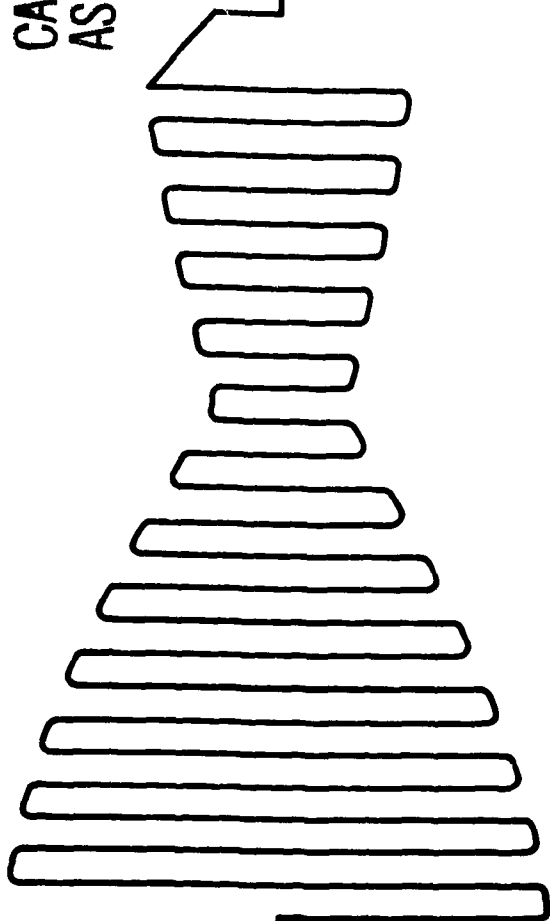
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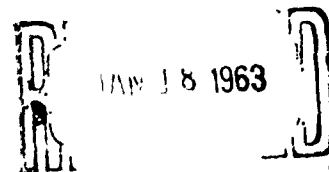
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RESEARCH IN FLUORINE CHEMISTRY, PROGRESS  
REPORT FOR PERIOD 16 SEPTEMBER 1962  
TO 15 DECEMBER 1962

**ROCKETDYNE**

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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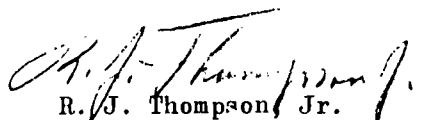
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## FOREWORD

The research effort described in this report was conducted by the Synthetic Chemistry Group of Rocketdyne's Research Department. This effort was supported by the Office of Naval Research under contract Nonr 1818(00) under the cognizance of Richard Hanson as Scientific Officer. Work accomplished for the period 16 September through 15 December 1962 is reported. Fulltime associates for this work were Dr. Howard H. Rogers, who was also Responsible Scientist, and Julian H. Johnson. The electrochemical interpretations were contributed by Dr. Sheldon Evans of the Physical Chemistry Group.

ABSTRACT

Data from the electrolysis of the  $\text{HF-N}_2\text{O}_4$ ,  $\text{HF-NO}$ ,  $\text{HF-N}_2\text{O}_4\text{-NO}$ ,  $\text{HF-N}_2\text{O}$  and the  $\text{HF-FNO}$  systems are correlated. It is concluded that the presence of  $\text{H}_2\text{O}$  in most systems, either as an initial component or as an electrolysis product, causes the same electrolysis products to form. New data on electrolyses in the  $\text{HF-N}_2\text{O}$ ,  $\text{HF-FNO}$ , and  $\text{HF-NH}_3$  systems are presented. It is suggested that the probable solubility of resulting F-N-O compounds in HF is accompanied by further electrolytic oxidation, thereby preventing their synthesis by electrolysis in HF.

A new procedure for the electrolytic drying of HF, based on current reversal, has been developed and is described. The results are compared with the old method.

The process of nickel dissolution at the anode during electrolysis is discussed and a hypothesis explaining observed phenomena presented.

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## INTRODUCTION

This report describes research which is a continuation of earlier work (Ref. 1) concerned with the electrochemical synthesis of compounds of nitrogen, oxygen and fluorine. This work had resulted in the synthesis of  $\text{NO}_3\text{F}$  and  $\text{O}_3$ . The systems which were studied included  $\text{HF-N}_2\text{O}_4$ ,  $\text{HF-NO}$ ,  $\text{HF-N}_2\text{O}$ , and  $\text{HF-NH}_3\text{-"O"}$ . The results of new work in the latter two systems and in the  $\text{HF-FNO}$  system are reported.

The study of electrode processes, which has been of considerable help in the interpretation and planning of experiments, has continued. The new data and interpretations are presented in this report.

## DISCUSSION

### ELECTROCHEMICAL SYNTHESIS

The effort this quarter has been concerned with the electrolyses in the  $\text{HF-N}_2\text{O-NaF}$ ,  $\text{HF-FNO}$  and  $\text{HF-NH}_3$  system. In addition, a new and effective procedure for the electrolytic drying of HF has been developed. The results of this work are discussed in the following sections and summarized in Table 1.

#### Drying of "Anhydrous" HF

The electrolytic drying of "anhydrous" HF as drawn from commercial cylinders is necessary if electrolyses are to be carried out in truly anhydrous systems. According to Burdon and Tatlow (Ref. 2), the drying of HF by electrolysis causes a reduction in current until the conductivity is almost zero when complete drying has occurred. Our experience with electrolytic drying showed that gradual passivation of the nickel anode accompanied by incomplete drying occurred. This passivation has been shown to occur during "drying" experiments in two ways. First, the measured anode potential was very high whereas the cathode potential remained relatively low. Since our reference electrode is closer to the anode than to the cathode, low conductivity in the solution would have been reflected in high apparent cathode potentials caused by the large voltage drop in the solution. Secondly, it was observed that the overall cell resistance markedly decreased when the cell was permitted to stand for a few minutes after the apparent completion of electrolytic drying. This effect can readily be seen by examination of the curves (Fig. 1).

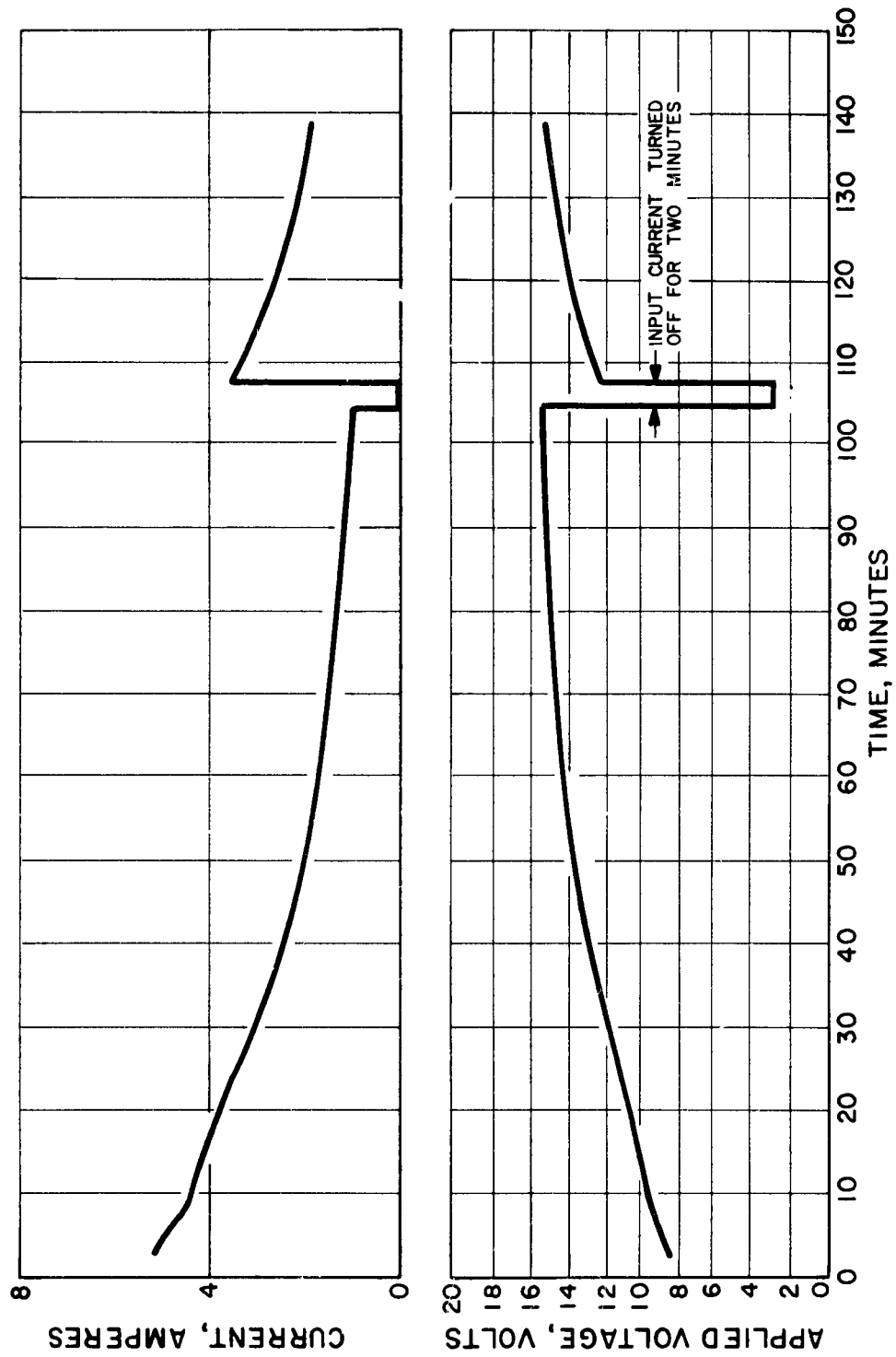
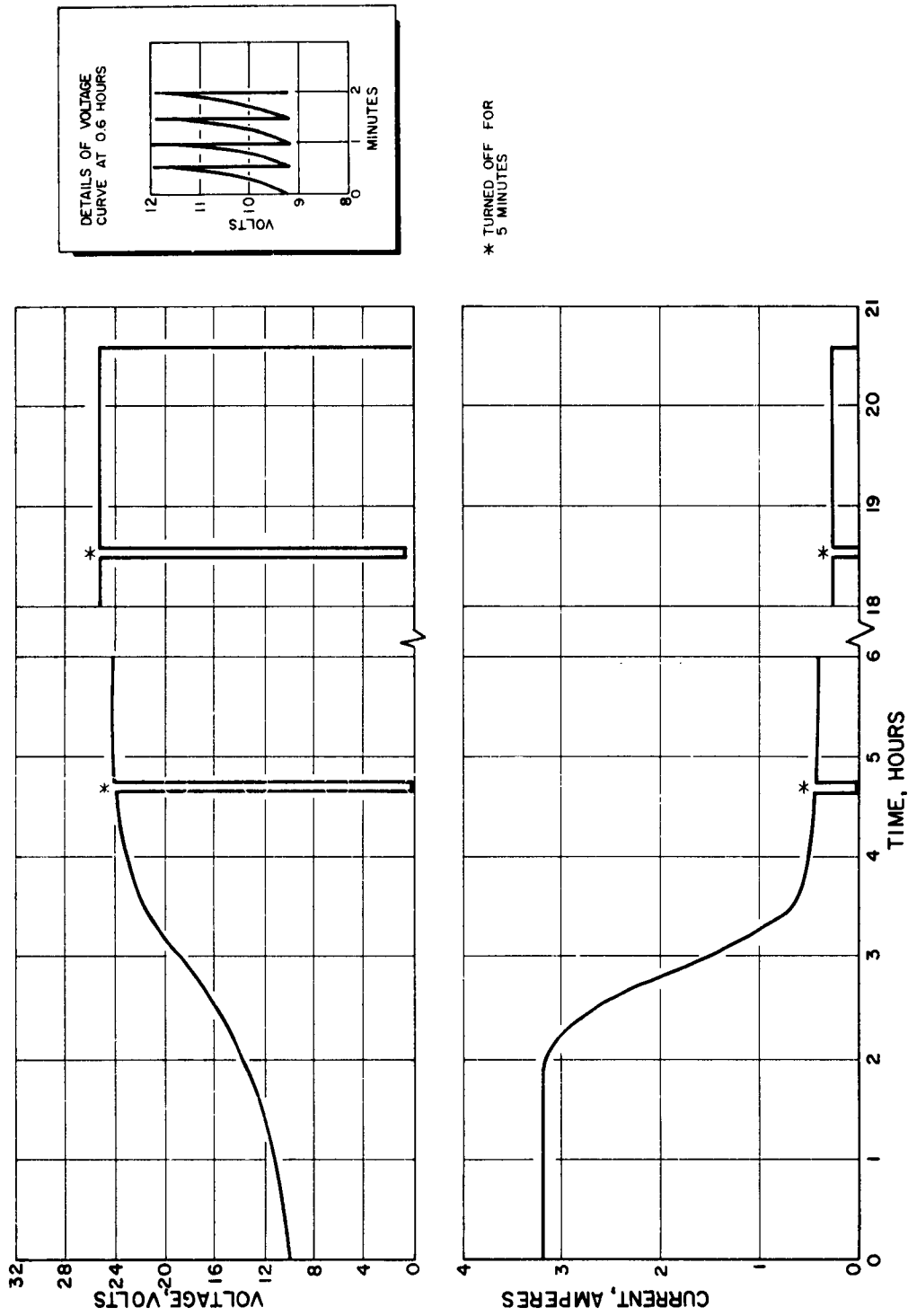


Figure 1. Typical Run. Electrolytic Drying of HF Without Reversal (A534-13)

After the resumption of electrolysis for a period, the phenomenon was repeated. It was hypothesized that, during drying, the severe anodic polarization was caused by the buildup of a gas film. When the electrode was permitted to stand without the passage of current, the gas film dispersed.

One approach tried was drying at a current density sufficiently low to prevent the occurrence of passivation. Unfortunately an excessive drying period was required, accompanied by severe corrosion of the anode.

The drying method developed has been quite successful. It depends on preventing excessive polarization by reversal of current flow, thereby permitting more current to flow at lower potentials than is possible without reversal. A device (described under Experimental Details) was built which was set to reverse the current flow to the cell each 30 seconds. In a typical experiment using this device, the cell resistance increased by a factor of 15 during the electrolysis. It was found that the overall cell conductivity did not increase upon turning off the current for 5 minutes (Fig. 2) indicating that the low cell conductivity was a result of actual drying rather than passivation. This conclusion is supported by a run in the  $\text{HF-NH}_3$  system, A534-22, because no oxygen-containing products were detected. In all earlier runs in the system, whether dried (no current reversal) or not, oxygen-containing products like  $\text{OF}_2$  and  $\text{NO}_2\text{F}$  were always found. The current and voltage curves as shown (Fig. 2) represent average values. The typical polarization curves found with each 30-second reversal period are also reproduced (Fig. 2). The current at this time (0.6 hours) was held constant so the polarization was observable only in the voltage readings.



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Figure 2. Typical Run, Electrolytic Drying of HF with Current Reversal (A534-73)

This reverse drying procedure has been used in all subsequent experiments where drying was desired. An overnight period provided more than sufficient time to achieve complete drying.

The System HF-NH<sub>3</sub>-NO

The system HF-NH<sub>3</sub>-NO was studied to determine if the presence of added oxygen as NO would have an effect upon electrolysis different from that of the oxygen normally present in HF as an impurity. The products, Run A534-15, Table 1, were the same as those obtained in earlier runs (Ref. 1).

The System HF-N<sub>2</sub>O-NaF

Additional experiments were conducted in the HF-N<sub>2</sub>O-NaF system to determine the effect of changing some of the experimental variables. These variables included electrode preparation, use of a porous Teflon divider (Ref. 1), and reverse current drying. In all runs the products were NF<sub>3</sub>, NO<sub>3</sub>F, and OF<sub>2</sub>. No definitive differences in the results of the three runs (Table 1) could be found. Earlier runs (Ref. 3) indicated that NF<sub>3</sub> was the only product found in greater than trace amounts, whereas in these later runs NO<sub>3</sub>F and OF<sub>2</sub> were also detected in two instances. The reasons for the differences in products is not clear.

The system HF-FNO

A solution of FNO in HF was prepared by the reaction of NOCl and HF (Ref. 4). The product, a mixture of FNO·3HF and FNO·6HF, was identified by its boiling point curve.

TABLE 1

## ELECTROLYSIS DATA\*

Number	Reactants	Mole Ratio	Internal Cell Temp, C	Current, Amperes	Potential, Volts	L of Mi
A534-13	HF (Drying)	---	-16 to -8	5.2 - 0.96	8.0 - 15.4	
A534-21	HF (Drying)**	---	---	5.6 3.2	7.8 - 10.0 8.0 - 15.0	
A534-22	HF-NH <sub>3</sub>	15:1	-14	0.75	5.3 - 4.8	
A534-15	HF-NH <sub>3</sub> -NO	14:1:(sat)	-12	0.75	4.5	
A534-16	HF-N <sub>2</sub> O (6 percent NaF)	Saturated Solution	-12 -12	2.5 2.5	5.0 4.9	
A-534-23	HF-N <sub>2</sub> O (6 percent NaF)	Saturated Solution	-13	0.5 2.5 0.5 2.5	5.2 5.8 5.0 5.8	
A534-26	HF-N <sub>2</sub> O (3 percent NaF)	Saturated Solution	-15 -8 -13	2.5 6.0 0.5	5.7 7.2 - 6.5 5.0	
A534-28	HF-FNO	19:1	-13 to -8	4.0	7.2 - 6.5	
A534-30	HF-FNO	16:1	-11 -4	2.0 8.0	5.6 - 4.6 6.8 - 5.8	

\*All runs conducted using mechanically cleaned electrodes. New anode used in A534-31 and

\*\*Reverse Current Drying of HF

2

TABLE 1

ELECTROLYSIS DATA\*

t, s	Potential, Volts	Length of Run, Minutes	Products		Remarks
			Principal	Trace	
16	8.0 - 15.4	100	OF <sub>2</sub>	CF <sub>4</sub>	
	7.8 - 10.0	175	OF <sub>2</sub>	CF <sub>4</sub> , NO <sub>3</sub> F, OF <sub>2</sub>	
	8.0 - 15.0	190			
	5.3 - 4.8	120	NF <sub>3</sub>	CF <sub>4</sub>	**
	4.5	90	OF <sub>2</sub> , NF <sub>3</sub> NO <sub>3</sub> F, N <sub>2</sub> O CF <sub>4</sub>	SO <sub>2</sub> F <sub>2</sub>	Divided Cell - Liquid Phase
	5.0	60	NF <sub>3</sub>	NO <sub>3</sub> F, OF <sub>2</sub>	Divided Cell - Liquid Phase
	4.9	60	None	None	HF dried overnight at 0.5 amps
	5.2	60	NF <sub>3</sub>	NO <sub>3</sub> F	Divided Cell - Liquid Phase
	5.8	60	NF <sub>3</sub> , OF <sub>2</sub>	NO <sub>3</sub> F	**
	5.0	30	NF <sub>3</sub>	None	
	5.8	15	NF <sub>3</sub>	NO <sub>3</sub> F	
	5.7	47	NF <sub>3</sub>	OF <sub>2</sub>	Divided Cell - Liquid Phase
	7.2 - 6.5	15	NF <sub>3</sub> , NO <sub>3</sub> F	OF <sub>2</sub>	**
	5.0	65	NF <sub>3</sub>	NO <sub>3</sub> F	
	7.2 - 6.5	42	OF <sub>2</sub>	N <sub>2</sub> O, NO <sub>3</sub> F, CF <sub>4</sub>	** HF dried for 35 min only
	5.6 - 4.6	70	NO	N <sub>2</sub> O, NO <sub>2</sub>	Divided Cell - Liquid Phase
	6.8 - 5.8	30	NO		HF Not Dried

\* anode used in A534-31 and -35; new cathode, A534-35



TABLE 1

(Continued)

Number	Reactants	Mole Ratio	Internal Cell Temp, C	Current, Amperes	Potential, Volts	Length of Run, Minutes
A534-31	HF-FNO	18:1	-14	2.0	4.7 - 5.4	70
			-7	8.0	7.0 - 10.8	30
A534-33	HF-FNO	19:1	-10	2.0 - 1.4	5.0 - 5.2	85
			-9 to -3	8.0	7.0 - 9.2	34
A534-35	HF-FNO	35:1	-16	2.0	6.0	80
			-13	4.0	5.8 - 7.3	75

\*\*Reverse Current Drying of HF

TABLE 1

(Continued)

2

Potential, Volts	Length of Run, Minutes	Products		Remarks
		Principal	Trace	
4.7 - 5.4	70	$N_2O$ , $NO_2$ , $CF_4$	$SO_2F_2$	Divided Cell - Liquid Phase
7.0 - 10.8	30	$NO$	$N_2O$	**
5.0 - 5.2	85	$NO$	$N_2O$ , $CF_4$	**
7.0 - 9.2	34	$NO$ , $N_2O$		
6.0	80	$NO$	$N_2O$	**
5.8 - 7.3	75	$NO$	$N_2O$ , $NO_2$	

Electrolyses in the system HF-FNO were run under several different conditions as listed (Table 1). In all but the first run only reduction products of the  $\text{NO}^+$  ion were found. Apparently there were also traces of a gas containing fluorine but attempts at identification have thus far been unsuccessful. The reason for the different products found in the first run is unknown.

According to Seel (Ref. 4), the electrolysis of HF-FNO solutions in a cell containing a diaphragm which was capable of separating the gaseous products should result in NO and  $\text{F}_2$  as products. In our cell, where no separation of the gaseous products is attained, the spontaneous reaction of NO and  $\text{F}_2$  to give FNO would be expected, which would, no doubt, dissolve in the electrolyte. The NO which was found as a product was probably a result of insufficient  $\text{F}_2$  being available. This shortage of  $\text{F}_2$  was caused by part of the current going to the dissolution of nickel (to make  $\text{NiF}_2$ ) at the anode rather than the generation of fluorine.

The synthesis of  $\text{N}_2\text{O}$  at the cathode is readily explained. It would be expected that the  $\text{NO}^+$  ion would reduce directly to NO, although, with a sufficiently high cathode potential, reduction to  $\text{N}_2\text{O}$  could also occur. The polarization curves (Fig. 3) which were taken before the start of the run show clearly that a second reaction takes place at the cathode at currents over one ampere. The anodic curve is, incidentally, similar to the polarization curve reported earlier for the HF-NO system (Ref. 3, Fig. 7).

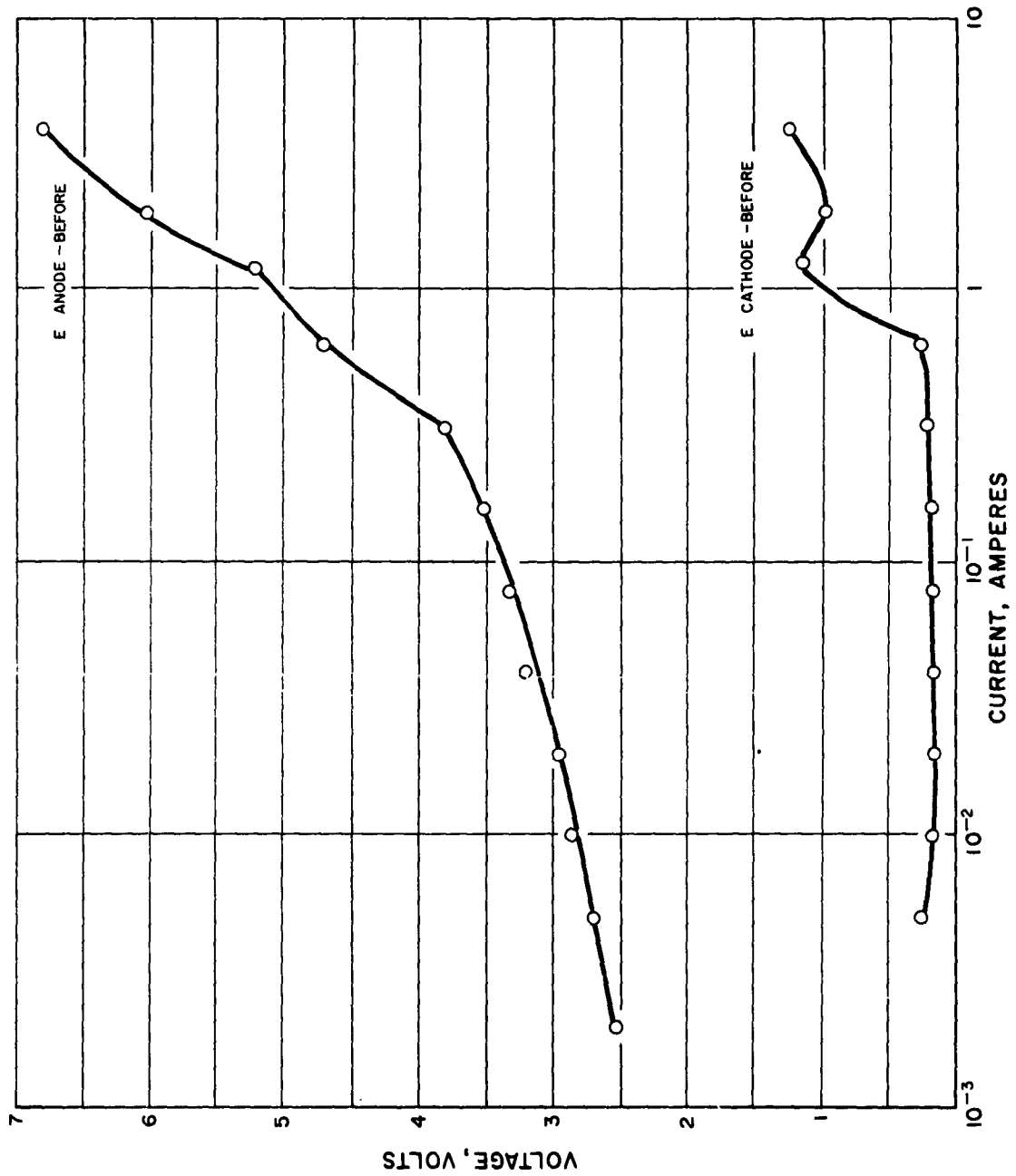


Figure 3. Polarization Curve HF-FNO (A534-36)

## ELECTRODE PROCESSES

Experiments were undertaken to study more closely electrode effects in anhydrous HF systems. Here interest was focused on the nature of the surface film on the electrode, the proportion of the current which contributed to the anodic dissolution process, and on gaining further insight into what was occurring in the "supposed" conventional electrolytic drying of HF.

### Metal Dissolution, General

The corrosion rates of nickel in the systems HF, HF-NaF, and HF-N<sub>2</sub>O<sub>4</sub> were determined under conditions identical to those prevailing during electrolysis experiments, but without the application of external current (i.e. open circuit corrosion rate). Since previous experiments had shown that the corrosion rate, as determined from weight loss measurements, was too low to obtain reasonable results in a short time period, it was decided to leave the nickel specimens in the solution for arbitrary periods greater than 12 hours.

The nickel specimen immersed in these systems was composed of local anodes and local cathodes. The magnitude of electrochemical corrosion was determined by the relative area of anodes to cathodes and by the energetics of reactions which occurred at each area. In this system, nickel dissolution occurred at anodic sites while hydrogen evolution occurred at cathodic sites. The rate of hydrogen evolution is frequently used to determine accurately metal dissolution rates (Ref. 5 and 6). Qualitatively, if the energetics of oxidation and reduction are favorable, much corrosion ensues. If reduction occurs with ease (good cathode areas) while the anodic oxidation or dissolution process is hindered, the process is said to be under anodic control; the over-all potential will lie close to that of the

cathode. Under such conditions, the corrosion rate can be increased by increasing the area of the anode and by the addition of an anodic depolarizer which bypasses or accelerates the slow step in the oxidation process. An excellent discussion of mixed potential theory relating to such processes was presented by Mears (Ref. 7).

It is convenient to express weight loss in terms of an equivalent current generally called the corrosion current ( $i_c$ ). This is in accord with a practice accepted for expressing electrochemical corrosion data. Since

$$\frac{\text{observed weight loss}}{\text{equivalent weight of nickel}} = \text{Number of equivalents} \quad (1)$$

and

$$i_c \times \text{time (seconds)} = \text{coulombs} \quad (2)$$

Combination of equations 1 and 2 with the statement of Faraday's law yields

$$\frac{i_c \times \text{time (seconds)}}{96,500} = \frac{\text{observed weight loss}}{29} \quad (3)$$

Rearrangement of equation 3 leads to an expression for  $i_c$ ,

$$i_c = \frac{\text{observed weight loss}}{29 \times \text{time (seconds)}} \times 96,500 \quad (4)$$

The corrosion currents thus calculated for nickel in the three systems are presented in Table 2. The corrosion current density, a value more useful for other researchers, was obtained by dividing the corrosion current by the measured surface area of nickel exposed to the solution.

There was no evidence of corrosion in any of the systems. At best, the values of Table 2 are rough figures since, with such low rates, numerous replicate experiments would be necessary to establish a statistical average. Each of the values is an average of results with two electrodes; the results within each set agreed within 10 percent.

The significance of these results can be appreciated if they are considered in light of electrochemical corrosion theory. If the corrosion reaction (the anodic dissolution of nickel) were under cathodic control, then addition of a cathodic depolarizer such as  $N_2O_4$  would have markedly enhanced the anodic dissolution rate. Since the corrosion rate was not affected by this addition (Table 2), it is reasonable to conclude that the corrosion process was not under cathodic control. An increase in solution conductivity would normally increase the corrosion current. The addition of NaF or  $N_2O_4$  increased the conductivity of the systems by a factor of at least 1,000. The corrosion rate was not markedly affected by such additions which also increased the fluoride ion concentration. Under these conditions, it was reasonable to conclude that the corrosion process was unaffected by changes in conductivity or fluoride ion concentration.

Dissolution of nickel at anodic areas probably resulted in a tightly bound insoluble film of nickel fluoride which then became a more noble cathodic site. If this film were not tightly bound to the nickel surface, further anodic areas would have been set up and the corrosion rate would have been higher. Under such conditions, increase of solution conductance could have influenced the corrosion rate. Such extremely low corrosion rates are explained by the diminishing number of electrochemical cells caused by the stifling of anodic sites.

The mixed potential of nickel in these systems was only slightly anodic to that of platinum immersed in the same system, confirming the view that the electrochemical mechanism was under anodic control. Visually, the nickel specimens appeared unattacked. The film which formed on the surface was thin, transparent and uniform. It could not be removed by wiping or by steam but was removed by abrasion.

#### Metal Dissolution During Electrolytic Drying

The current equivalent of the nickel weight loss ascertained under conditions of drying with and without current reversal is shown in Table 3.

It can be seen that the rates of nickel dissolution were of the same order of magnitude for the two drying procedures. Thus the effect of current reversal had little to do with the nickel dissolution process, or with the prevention or breakdown of a solid film. Film breakdown and subsequent regeneration would have resulted in markedly greater rates of nickel dissolution. The depolarization resulting from current reversal was probably a combined effect of partially obviating concentration polarization and gas film polarization.



TABLE 2

CORROSION RATE OF NICKEL IN ANHYDROUS HF MEDIA

System	Corrosion Current $i_c$ (ma)	Corrosion Current Density $\mu\text{a/cm}^2$
HF	0.2	1.7
HF-NaF	1.0	8.0
HF-N <sub>2</sub> O <sub>4</sub>	0.26	2.3

TABLE 3

CURRENT EQUIVALENT OF THE WEIGHT LOSS OF NICKEL DURING ELECTROLYTIC DRYING

Run	Current Equivalent of Weight Loss (amps)	Current Density (ma/cm <sup>2</sup> )
534-13 (no reversal)	0.32	2.74
A534-21 (reversal)	0.36	3.1
A534-27 HF-NaF (reversal)	0.42	3.7

TABLE 4

CURRENT EQUIVALENT OF THE WEIGHT LOSS OF  
NICKEL IN HF-N<sub>2</sub>O<sub>4</sub> DURING ELECTROLYSIS

Run	Electrolysis Current (amps)	Electrolysis Current Density (ma/cm <sup>2</sup> )	Current Equivalent of Weight Loss (ma/cm <sup>2</sup> )
A534-18	0.8	6.9	.112
A534-20	8.0	69	.112

Metal Dissolution HF-N<sub>2</sub>O<sub>4</sub> System

The current equivalent of the nickel weight loss determined in HF-N<sub>2</sub>O<sub>4</sub> at two different applied current densities is shown in Table 4.

In a previous discussion of the anodic polarization curve of nickel it was postulated that, below the apparent limiting current, nickel was dissolving in accordance with Faraday's Law. The electrolyses at 0.8 amps and 8.0 amps represent electrolysis experiments carried out below and above the limiting current respectively. Below the limiting current the products which form are oxygen and OF<sub>2</sub>. Nickel is not dissolving quantitatively in accordance with Faraday's Law below the limiting current. It is reasonable to conclude that the rise in potential which occurs at the limiting current is due to gas film polarization which results in the formation of ozone. It was observed that anodic depolarization occurred after ozone was produced, indicating that the reaction which now occurs favors the decrease in gas film polarization.

Nickel was dissolving at a rate far lower than the applied currents used in the electrolysis experiments. The rate of nickel dissolution is independent of the applied current in this region which indicates that nickel dissolution is rate-limited through a tightly adhering film and that in no case is an electrolysis carried out at a nickel surface.

In practice, the HF or HF-NaF solution was electrolytically dried using the current reversal technique. The nitrogen-oxygen species was then introduced and electrolysis started. Under such conditions it was difficult to determine just what portion of the current was used for nickel dissolution in each of the processes (i.e. drying and electrolysis). Knowledge of a reasonable value for the current equivalent of the weight

loss permits the determination of the dissolution rate of nickel during electrolysis. To demonstrate this, it may be convenient to work backward. In Runs A534-23 and A534-26, the HF-NaF was dried prior to the addition of  $N_2O$  and subsequent electrolysis. It is reasonable to assume that during the electrolysis the cathode weight loss was negligible with respect to the anode weight loss. The ultimate change in cathode weight loss is then assumed to be the change caused by current reversal drying. The values calculated from this procedure for the current equivalent of the weight loss during drying (3.6 and 5 ma/cm<sup>2</sup>, Runs A534-23 and A534-26 respectively) are well in agreement with independent experiments (Table 3).

It is now possible to estimate the amount of current which aids the nickel dissolution during electrolysis. The total anode weight loss is a result of both drying and electrolysis. Estimating that which results from drying permits us to estimate the portion of the current used in the nickel dissolution process during electrolysis. The electrolyses, A534-23 and A534-26, were carried out at several currents. However, in both cases the calculated value for the current equivalent of the weight loss during electrolysis was only a small portion of the current used.

The film which formed on open circuit in HF, HF-NaF, or HF-N<sub>2</sub>O<sub>4</sub> was not sufficiently thick to insulate the electrodes and prevent passage of current. In addition, nickel dissolution occurred at the anode with the application of current. The dissolution process in HF-NaF and HF was different from that in HF-N<sub>2</sub>O<sub>4</sub>. It can be seen from the tables that on anodic polarization nickel dissolved at a far lower rate in HF-N<sub>2</sub>O<sub>4</sub> than in HF or HF-NaF. It is certain that the nature of the film present on anodic polarization is different, but it is not certain that it is related to the strength of the oxidizing agent. Previous experiments did indicate

that it was possible, under certain conditions, to dissolve an appreciable amount of nickel in the HF-NO system, and the rate of weight loss in the HF-N<sub>2</sub>O system was greater than that in the HF-N<sub>2</sub>O<sub>4</sub> system.

Estimation of current equivalents of the weight loss allows for rough calculation of the uses of each part of the current. It is concluded that only a small portion aided in the nickel dissolution process. A small percent accounted for the OF<sub>2</sub>, and N-O-F compounds formed. The bulk of the current was used in the production of oxygen.

## EXPERIMENTAL DETAILS

### DRYING OF HF

The procedure in drying HF by the reverse drying method differed from normal electrolyses (Ref. 8) only in the use of the automatic reversing switch described below.

In a typical run using approximately 250 milliliters of HF drawn directly from the cylinder (Matheson) as a liquid, the initial potential was 10 volts at a current of 3.2 amperes. The current was maintained at 3.2 amperes by the current regulator for five hours; during this time period the potential had risen to 15 volts. In the next 2-1/2 hours the current had decreased to 0.56 amperes while the voltage had risen to 25. No significant changes in conditions were found on continuing electrolysis or interrupting current for 5 minutes and then resuming electrolysis (Fig. 2).

### AUTOMATIC REVERSING SWITCH

The circuit for the automatic reversing switch is given in Fig. 4.. With the two relays as shown, both the current supply to the cell and the recording voltmeter connections were periodically reversed. With the component values given it has been possible to obtain either equal or unequal time periods which were continuously variable from one to forty seconds.

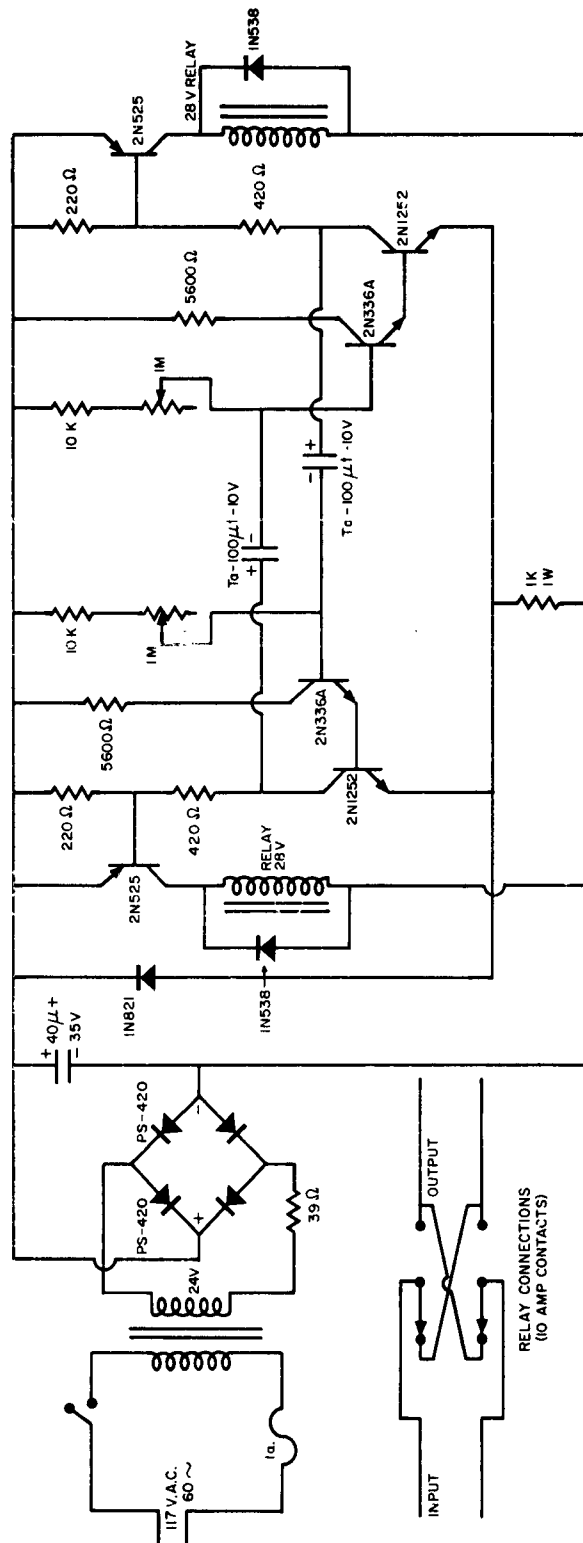
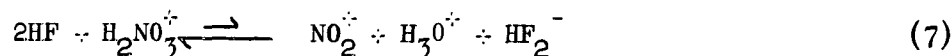
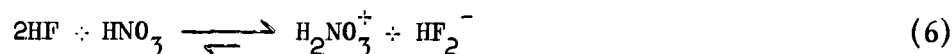
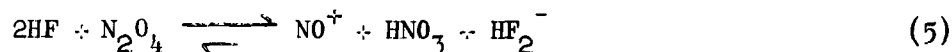


Figure 4. Automatic Reversing Switch

### CONCLUSIONS

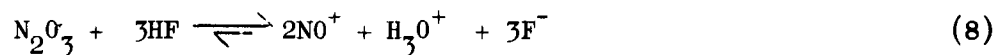
During the course of this project, a pronounced similarity in the nature of the products ( $\text{NO}_3\text{F}$ ,  $\text{OF}_2$ ) of electrolysis from several systems of HF with nitrogen-oxygen compounds has been observed. This similarity points to a corresponding similarity in the nature of the electrolytes. In the case of the  $\text{HF-N}_2\text{O}_4$  system, it has been postulated previously (Ref. 8) that the reactions represented in Eq. 5 and 6 below take place. In addition, it has been shown by infrared analysis of the solution that the reaction represented in Eq. 7 also takes place at least to a small extent (Ref. 9).



Equation 5 has been verified because distillation of the solution has led to the separation of  $\text{HNO}_3$  and  $\text{FNO}$  as complexes in HF (Ref. 10). The high conductivity of the  $\text{HF-HNO}_3$  system shows that ionization probably occurs according to Eq. 6 (Ref. 8). Electrolysis of the  $\text{HF-N}_2\text{O}_4$  system could then be viewed as the electrolysis of a mixture of the  $\text{HF-FNO}$ ,  $\text{HF-HNO}_3$ , and small amounts of the  $\text{HF-NO}_2\text{F}$  and  $\text{HF-H}_2\text{O}$ . It has been indicated from our work in this quarter with the  $\text{HF-FNO}$  system, that the products of electrolysis are principally  $\text{NO}$  and  $\text{F}_2$ . Because of the presence of a low concentration of water from the dissociation of  $\text{H}_2\text{NO}_3^+$ , Eq. 7,  $\text{OF}_2$  rather than  $\text{F}_2$  would be a product when  $\text{HF-N}_2\text{O}_4$  solutions are subjected to electrolysis. This situation was even more pronounced when the electrolysis

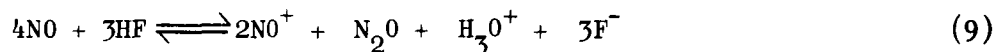


of HF-N<sub>2</sub>O<sub>4</sub>-NO was attempted (Ref. 3). According to Horn, Bartlett and Tivers (Ref. 9), the reaction of N<sub>2</sub>O<sub>3</sub> with HF may take place according to Eq. 8, yielding essentially a 2:1 mixture of FNO and H<sub>2</sub>O in HF.



Electrolysis of this solution would be expected to yield O<sub>2</sub> rather than OF<sub>2</sub> because of the presence of a large concentration of water. The presence of N<sub>2</sub>O<sub>4</sub> in the products strongly suggested the presence of elementary oxygen (2NO + O<sub>2</sub>  $\rightleftharpoons$  N<sub>2</sub>O<sub>4</sub>). Nitrogen tetroxide is not normally found in the products from the electrolysis of HF-N<sub>2</sub>O<sub>4</sub> solutions unless the mole ratio is such that N<sub>2</sub>O<sub>4</sub> is in excess.

Horn, Bartlett and Tivers (Ref. 9) also postulate the following mechanism for the reaction of NO with HF.



The work in this laboratory tends to at least partially confirm this equation because the products from the electrolysis of HF-NO, NO<sub>3</sub>F, and OF<sub>2</sub> (Ref. 3) were also found from the electrolysis of the system HF-N<sub>2</sub>O (Ref. 3 and this report). The synthesis of NF<sub>3</sub> in addition, in the latter system but not in the HF-NO system, does cast some doubt on the validity of Eq. 9. The following equation would seem to be a reasonable ionization scheme for the reaction.



The use of a three electrode system in determining polarization curves and monitoring electrode potentials during electrolysis has proved to be an extremely useful tool. While some of the electrode processes have

been at least partially unscrambled, yielding valuable information concerning the mechanisms of the reactions, it has become apparent that electrolyses in anhydrous hydrogen fluoride are quite complex. Furthermore very little coherent and precise data on this system has been accumulated prior to this research, rendering complete interpretations of our data very difficult. Since the interests of the researchers have been oriented primarily toward synthesis, an extensive study of the physical chemistry of electrolysis in anhydrous hydrogen fluoride did not seem warranted. Certainly, all the results to date have indicated that the synthesis of new compounds of oxygen, nitrogen and fluorine by this method would be unlikely with our current knowledge.

### SUMMARY

A new procedure for the electrolytic drying of HF has been developed. The procedure, which depends upon periodic current reversal to suppress polarization, has been found to remove water thoroughly from commercial HF (Matheson) giving an anhydrous solvent with low conductivity. It was shown that electrolytic drying without current reversal did not yield dry HF. The apparent low cell conductivity after electrolysis was shown to be caused by electrode polarization rather than by low solution conductivity.

The current equivalent of the weight loss determined for the two drying techniques (reversal and no reversal) was found to be on the order of a few milliamps per centimeter square, independent of the technique used. The depolarization observed during current reversal had little to do with the nickel dissolution process and probably resulted from a combined effect of partially obviating concentration polarization and gas film polarization.

The open circuit corrosion current of nickel in HF,  $\text{HF-N}_2\text{O}_4$ , and HF-NaF was determined to be a few microamperes per square centimeter. It was shown that the corrosion process was under anodic control; a tightly bound nickel fluoride film stifled anodic sites and accounted for low corrosion currents. These were independent of the solution conductivity, concentration of fluoride ion, and the presence of an efficient cathodic depolarizer.

The equivalent current for the weight loss of nickel was determined in the  $\text{HF-N}_2\text{O}_4$  system at two different currents, one above and the other below the limiting current noticed on the anodic polarization curve. The

equivalent currents were virtually identical which indicates that nickel was not dissolving in accordance with Faraday's Law below the limiting current. At any of the currents used in the electrolysis experiments only a small percentage was used in the nickel dissolution process.

A method for the estimation of the equivalent weight loss due to dissolution during drying alone and during other electrolyses, when the electrodes were weighed before drying and then after the electrolysis, was shown to work satisfactorily.

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